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(54) PRECOATED STEEL SHEET EXCELLENT IN DURABILITY

(57) Abstract:

PROBLEM TO BE SOLVED: To produce a precoated steel sheet excellent in corrosion resistance and scratching resistance.

SOLUTION: This precoated steel sheet uses a Zn-Al-Mg plated steel sheet provided with a plating layer

containing 4 to 10% Al, 1 to 4% Mg, 0.002 to 0.1% Ti and 0.001 to 0.45% B and having a surface fitted with fine ruggedness by the dispersion of Ti-Al based, Ti-B based and/or Al-B based precipitations, the control of the growth of a crystal grains, pickling roughening, mechanical roughening, or the like, as a precoated original sheet. After the plating layer is subjected to chemical conversion treatment, a coating film is formed.

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CLAIMS

[Claim(s)]

[Claim 1] Four to aluminum:10 mass %, one to Mg:4 mass %, 0.002 to Ti:0.1 mass %, and B:0.001 - 0.45 mass % are included. The good paint steel plate of the endurance characterized by for the remainder having the presentation of Zn substantially, preparing the plating layer to which the detailed irregularity whose arithmetical-mean-deviation-of-profile Ra is 0.5-5.0 micrometers was attached in the front face of a substrate steel plate, and forming the resin paint film through a chemical conversion coat on a plating layer.

[Claim 2] The paint steel plate according to claim 1 in which detailed irregularity is formed with the sludge of a Ti-aluminum system, a Ti-B system, and/or an aluminum-B system.

[Claim 3] The paint steel plate according to claim 1 in which detailed irregularity is formed with the crystal grain in which growth control was carried out by accommodation of cooling conditions.

[Claim 4] claims 1-3 in which detailed irregularity is formed by any one sort or two sorts or more of mechanical means of acid washing after hot dipping, brushing, dull processing, and shot blasting -- a paint steel plate given in any they are.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to corrosion resistance and the paint steel plate which scratched and was excellent in resistance.

[0002]

[Description of the Prior Art] After a paint steel plate used the plating steel plate of a zinc system or a zinc-aluminum system as a paint negative and pretreated spreading mold chromate treatment etc., its two quart type which formed the under coat paint film in consideration of the adhesion and corrosion resistance over a paint negative, and formed the finishing paint film which was further excellent in an appearance, weatherability, etc. was in use. However, recently, in order to aim at the simplification and cost cut of a production process, one quart-ization of a paint steel plate is advanced focusing on a household-electric-appliances device, inner package material, and the object for sheathing materials. If the plastic paint for under coats is used for one quart, the appearance after paint will tend to become orange peel-like, and the appearance which can be satisfied as a paint steel plate will not be acquired. Weatherability runs short in epoxy system plastic paint. Then, the plastic paint which raised the adhesion of the plastic paint for finishing paint or the coating for finishing is used as a coating for one quart. It is also known that corrosion resistance will be given to the coating for one quart by combination of a rust preventive pigment.

[0003]

[Problem(s) to be Solved by the Invention] Chromium system compounds, such as strontium chromate which discovers the outstanding rust-proofing ability as a rust preventive pigment, are used widely. However, since the paint film which blended the chromium system compound is easy to be colored yellow, constraint joins the addition of a chromium system compound and an one quart paint steel plate with sufficient corrosion resistance is not obtained. Although there are an ion-exchange silica, phosphate, etc. as rust preventive pigments other than the chromium system which does not color a paint film yellow, abundant addition is needed in order to acquire the corrosion resistance which all have low rust-proofing ability and is needed as compared with a chromium system rust preventive pigment. However, constraint joins the addition of a rust preventive pigment also in this case, and sufficient corrosion resistance is not acquired from gloss, weatherability, moisture resistance, etc. deteriorating in an one quart paint film, if abundant addition is carried out.

[0004] By the way, although the paint film which was excellent in an appearance or weatherability as compared with the under coat paint film will be formed if the conventional zinc system or a zinc-aluminum system plating steel plate is painted in the coatings for one quart, paint film adhesion is not enough and a paint film degree of hardness also becomes low. Therefore, effect is done and scratched to the adhesion of a paint film degree of hardness and a substrate, resistance falls, and a paint film life becomes short.

[0005]

[Means for Solving the Problem] This invention is thought out that such a problem should be solved,

and by using the plating steel plate with which the Zn-aluminum-Mg system plating layer which attached irregularity detailed as a paint negative was formed, it scratches, resistance is presented and it aims at the corrosion resistance which was excellent as compared with the conventional paint steel plate, and offering the good paint steel plate of endurance. The paint steel plate of this invention contains four to aluminum:10 mass %, one to Mg:4 mass %, 0.002 to Ti:0.1 mass %, and B:0.001 - 0.45 mass % in order to attain the object. The remainder has the presentation of Zn substantially, the plating layer to which the detailed irregularity whose arithmetical-mean-deviation-of-profile Ra is 0.5-5.0 micrometers was attached is prepared in the front face of a substrate steel plate, and it is characterized by forming the resin paint film through a chemical conversion coat on a plating layer. Detailed irregularity can be formed with acid washing after the crystal grain in which growth control was carried out by distribution of a Ti-aluminum system, a Ti-B system, and/or an aluminum-B system sludge, and accommodation of cooling conditions, and hot dipping, brushing, dull processing, shot blasting, etc.

[0006]

[Function] this invention person etc. did examination examination of various effects the shape of table planarity of the paint negative used as an one quart paint steel plate affects paint film adhesion and a paint film degree of hardness. Consequently, in the conventional zinc system or the zinc-aluminum system plating steel plate, the mechanical engagement (namely, anchor effect) with past [smoothness] and a paint film did not have an enough plating layer front face, and since the plating layer itself was elasticity comparatively, it was presumed that it was the cause of inadequate paint film adhesion or a paint film degree of hardness. Then, as a result of investigating the plating steel plate with which are satisfied of paint film adhesion and the demand characteristics of a paint film degree of hardness, it found out that a Zn-aluminum-Mg system plating steel plate was the optimal as an one quart paint steel plate.

[0007] a Zn-aluminum-Mg system plating steel plate shows the corrosion resistance which was markedly alike and was excellent with Mg contained in the plating layer. Moreover, if detailed irregularity is attached to a plating layer front face, an anchor effect will be discovered without degrading the appearance of an one quart paint film, and paint film adhesion will improve. Detailed irregularity is formed with distribution of a Ti-aluminum system, a Ti-B system, and/or an aluminum-B system sludge, growth control of plating layer crystal grain, acid washing after hot dipping, brushing, dull processing, shot blasting, etc. Especially, since a plating layer, as a result the one quart paint film itself are made hard with sludges, such as a Ti-aluminum system, a Ti-B system, and an aluminum-B system, it scratches, resistance is improved and the one quart paint steel plate excellent in endurance is obtained. Detailed irregularity contributes effective in improvement in paint film adhesion according to the same mechanism also not only to an one quart paint steel plate but to paint steel plates, such as two quart and three etc. quart.

[0008]

[Embodiment of the Invention] When attaching detailed irregularity to a plating layer front face with a Ti-aluminum system, a Ti-B system, and/or an aluminum-B system sludge, to the Zn-aluminum-Mg system plating steel plate used as a paint substrate aluminum: The plating layer in which the remainder has the presentation of Zn substantially is formed in the steel plate front face including four to 10 mass % (preferably five to 7 mass %), one to Mg:4 mass % (preferably 2.5 to 3.5 mass %), 0.002 to Ti:0.1 mass %, and B:0.001 - 0.45 mass %. This plating layer makes the ternary eutectic organization of aluminum/Zn/Zn₂Mg a matrix, and has the organization which a primary phase aluminum phase or a primary phase aluminum phase, and Zn single phase distributed to the matrix.

[0009] aluminum in a plating layer presents the operation which raises the corrosion resistance of a plating layer while controlling that dross occurs during the plating bath at the time of plating steel plate manufacture. Such an operation becomes remarkable with aluminum content more than 4 mass %. In aluminum content of under 4 mass %, the corrosion-resistant improvement effectiveness is not enough, and the operation which controls generating of magnesium-oxide system top dross falls, and it becomes the cause by which the smooth nature of a plating layer front face spoils a paint appearance bad. On the contrary, if aluminum of the excessive amount exceeding 10 mass % is contained, a Fe-aluminum

system alloy layer will grow up to be the interface of a plating layer and a substrate steel plate remarkably, and the workability and adhesion of a plating layer will fall. Consequently, when a paint steel plate is processed, it becomes easy to generate a big paint film crack and paint film exfoliation. [0010] Mg in a plating layer makes a plating layer front face generate homogeneity and a precise and stable corrosion product, and presents the operation which raises the corrosion resistance of a plating layer remarkably. Such an operation becomes remarkable with Mg content more than 1 mass %. Mg content cannot grow up to be a plating layer front face easily as a coat with a uniform corrosion product under by 1 mass %, and the corrosion-resistant improvement effectiveness is not enough. Conversely, if Mg of the excessive amount exceeding 4 mass % is contained, it will be easy to generate about [that the corrosion-resistant improvement effectiveness of having balanced loading of Mg is saturated], and magnesium-oxide system top drop during a plating bath, and it will become the cause of degrading the appearance of a paint steel plate. Moreover, in Mg content exceeding 4 mass %, the workability of a plating layer falls, and when a paint steel plate is processed, it becomes easy to generate a big paint film crack.

[0011] Ti and B present the operation which controls generation and growth of Zn₁₁Mg₂ phase at the time of hot dipping. Zn₁₁Mg₂ phase is observed as a pattern that it was conspicuous when it was distributed over the plating layer, since gloss was high, and degrades the appearance of a paint steel plate. Zn₁₁Mg₂ phase has an adverse effect also on corrosion resistance. Generation and growth of Zn₁₁Mg₂ phase are notably controlled by Ti addition more than 0.002 mass %, and/or B addition more than 0.001 mass %, and is suppressed by extent to which the irregularity of a plating layer front face does not have an adverse effect on the appearance of a paint steel plate. However, if Ti content exceeds 0.1 mass %, the sludge of a Ti-aluminum system will grow into a plating layer, and it will become easy to produce the strong irregularity which degrades the appearance after paint on a plating layer front face. Even when B content exceeds 0.045 mass %, sludges, such as a Ti-B system and an aluminum-B system, grow into a plating layer, and it becomes easy to produce the strong irregularity which degrades the appearance after paint on a plating layer front face.

[0012] Sludges, such as a Ti-aluminum system exposed on a plating layer front face, a Ti-B system, and an aluminum-B system, give about [surface roughness Ra:1micrometer] detailed irregularity to a plating layer front face. Detailed irregularity is irregularity which is not seen, enlarges a touch area with processing liquid at the time of chemical conversion, and makes the chemical conversion coat excellent in adhesion form in the plating layer of the conventional zinc system or a zinc-aluminum system. The plating layer front face where the Ti-aluminum system, the Ti-B system, the aluminum-B system, etc. deposited is hard as compared with the plating layer of the conventional zinc system or a zinc-aluminum system. Since a paint film is formed in a plating layer front face with hard detailed irregularity, an anchor effect is fully demonstrated and paint film adhesion improves conjointly with a thing with a big touch area. The plating layer made hard by the deposit of a Ti-aluminum system, a Ti-B system, an aluminum-B system, etc. is scratched as compared with the plating layer of a zinc system or a zinc-aluminum system, and resistance also becomes high.

[0013] The irregularity with a detailed plating layer can be formed with adjustment of the cooling conditions at the time of hot dipping, acid washing after hot dipping, brushing, dull processing, shot blasting, etc. If the cooling rate of a plating layer is slow, the crystal grain of the ternary eutectic organization of aluminum/Zn/Zn₂Mg will grow greatly, and the irregularity of a plating layer front face will become sparse with a fraction and an ununiformity. On the other hand, if a cooling rate is gathered, crystal grain makes it detailed, surface irregularity will be a large number, and will become uniformly precise, and the improvement effectiveness in the adhesion force will become remarkable. Since crystal grain becomes detailed, the plating layer itself is made hard. The approach of spraying the cooling water which added ammonium phosphate etc. in air cooling by an air-jet cooler etc., water, or water on cooling of a plating layer is employable.

[0014] If a plating layer front face is etched from an acid etc., the Zn₂Mg phase which is easy to dissolve in an acid will be etched preferentially, and detailed irregularity will be formed in a plating layer front face. On the other hand, in order that a Ti-B system, a Ti-aluminum system, and an

aluminum-B system sludge may remain in the plating layer front face after etching, the degree of hardness of a plating layer front face rises. There are a hydrochloric acid, a nitric acid, etc. in the acid used for etching. Irregularity can also be given to a plating layer front face by approaches, such as a mechanical approach, for example, brushing, dull processing, and blasting. In this case, soft aluminum phase and Zn phase are removed preferentially, or soft aluminum phase and Zn phase are pressed down with a dull roll etc., and in order that the hard sludge of a Ti-B system, a Ti-aluminum system, and an aluminum-B system may remain, a plating layer front face makes it hard. The irregularity of a plating layer front face is changeable like other plating material with the surface roughness of a dull roll, the construction material of an abrasive material or a shot blasting agent, and particle size.

[0015] Detailed irregularity effective in improvement in the paint film adhesion which originated in touch-area buildup with the anchor effect and plating layer front face to a paint film, and a paint film by the various approaches explained above is attached to a plating layer front face. The improvement effect of paint film adhesion becomes remarkable when arithmetical-mean-deviation-of-profile Ra adjusts irregularity to the range which is 0.5-5.0 micrometers. $Ra < 0.5$ micrometer is not enough as the improvement effectiveness in adhesion by detailed irregularity, in $Ra > 5.0$ micrometer, irregularity becomes large too much and an appearance tends to deteriorate.

[0016] If the plating steel plate with which the Zn-aluminum-Mg plating layer with the front face which attached detailed irregularity was formed is used for a paint negative, a poorly soluble corrosion product precise [aluminum and Mg in a plating layer] and stable will be generated. A corrosion product is distributed over the interface of a plating layer and a paint film, and works as barrier which covers the corrosive ion which advances from the outside. Therefore, as for the corrosion resistance of a flat part, paint film blistering and rust generating are suppressed from the first in the section with a paint film crack, amputation stump sides, or those near. Compatibility of a corrosion product with a chemical conversion coat and a paint film is high, and also when raising paint film adhesion, it is effective.

[0017] Although a Zn-aluminum-Mg system plating steel plate is painted with a continuation paint line like the conventional paint steel plate, in advance of paint, chemical conversion of the plating layer front face is carried out, and a chromate system coat or a chromium free coat is formed. In order to contact a plating layer front face in chromic-acid system processing liquid or phosphoric-acid-chromic-acid system processing liquid and to secure corrosion resistance and paint film adhesion in chromate treatment, it is desirable to form the chromate film of the chromium conversion coating weight 5 - 100 mg/m². As a chromate film, water solubility or water-dispersion resin, and a silica can be included.

[0018] In chromium free processing, the processing liquid which added suitably resin, colloidal silica, an inorganic acid, an organic acid, a fluoride, a silane, or titanium rise ring material is used for metallic oxides, such as a silica system, a manganese system, a phosphoric-acid system, a titanate-acid system, and a zirconic acid system. A chromium free coat is formed so that the total amount of coats may serve as 10 - 500 mg/m² preferably. Moreover, it is desirable to carry out surface control suitably by nickel deposit processing etc. on the occasion of chromate treatment or chromium free processing.

[0019] An one quart paint film is formed in the front face of the Zn-aluminum-Mg system plating steel plate by which chemical conversion was carried out. An one quart paint film is formed by the same approach as the conventional zinc system or a zinc-aluminum system plating steel plate. The coating for one quart paint films is prepared by blending a rust preventive pigment with polyester resin, epoxy denaturation polyester resin, a fluoro-resin, acrylic resin, urethane resin, etc. a color pigment and if needed. There is metallic pigment, such as titanium oxide, carbon black, cyanine blue, cyanine Green, an iron oxide, and an aluminium powder or luminosity powder, in a color pigment. There are non-chromium system rust preventive pigments, such as a chromium system rust preventive pigment represented by strontium chromate, titanium oxide, polyphosphoric acid aluminum, and calcium silicate, among the rust preventive pigments.

[0020] Various add-in material and the various aggregates, such as an antimicrobial agent, an antifungal agent, an insecticide, a non-binder, lubricant, a dirt inhibitor, and a flatting, an extender, powder, etc. may be added in coatings if needed. It is also possible to form a clear paint film, without stopping the addition of a pigment or adding a pigment. The coating for one quart paint films is applied to a plating

layer front face by the coverage from which desiccation thickness is preferably set to 0.1-20 micrometers, and printing and hardening of it are done according to a conventional method. Or an one quart paint film can also be formed in a plating layer front face by the laminating method. fine -- the improvement effectiveness in paint film adhesion by **** irregularity is not what was restricted to the one quart steel plate, and is effective also to two quart and a three quart steel plate. In this case, the coating which prepared the additive to various resin and attached the color tone (also including a clearance) of arbitration to it like the paint film of the 1st quart is used for the paint film of the 2nd quart and the 3rd quart, and it is formed with the thick film of arbitration.

[0021]

[Example 1] The Zn-aluminum-Mg system plating steel plate of plating coating weight 70 g/m² was manufactured with the continuation hot-dipping line of a ZENJIMIA method per 0.5mm of board thickness in which the plating layer of the presentation shown in a table 1 was formed, and one side. When the front face of the obtained plating steel plate was observed, in the test numbers 1-9 with which intermetallic compounds, such as a Ti-aluminum system, a Ti-B system, and an aluminum-B system, deposited, the plating layer with the front face where the detailed irregularity of 0.6-2.1 micrometers of Ra was attached was formed. On the other hand, with the test numbers 10-15 without a deposit of an intermetallic compound, the irregularity of a plating layer front face had stopped at 0.2-0.4 micrometers of Ra.

[0022]

表 1 : めっき層の組成及び表面の凹凸

試験 No.	めっき層の組成 (質量%)					めっき層 表面の凹凸 Ra (μm)	区 分
	Zn	Al	Mg	Ti	B		
1	残部	6	3	0.02	0.008	1.2	本 発 明 例
2	残部	6	1	0.02	0.008	1.3	
3	残部	4	3	0.02	0.008	0.6	
4	残部	4	1	0.02	0.008	0.9	
5	残部	9	3	0.02	0.008	1.9	
6	残部	9	1	0.02	0.008	2.1	
7	残部	6	3	0.02	0.008	1.2	
8	残部	6	3	0.02	0.008	1.2	
9	残部	6	3	0.02	0.008	1.2	
10	残部	0.2	—	—	—	0.2	比 較 例
11	残部	5	3	—	—	0.3	
12	43.4	55	—	—	—	0.4	
13	残部	0.2	—	—	—	0.2	
14	残部	0.2	—	—	—	0.2	
15	残部	0.2	—	—	—	0.2	

[0023] After carrying out surface control of each plating steel plate, it washed and dried by hot water rinsing and rinsing. Subsequently, it was made to dry at 100 degrees C, without having applied spreading mold chromate treatment liquid (Nippon Paint Co., Ltd. make surfboard coat NRC300NS) to the plating steel plate, and rinsing it by the roll coater, and the chromium conversion coating weight of

40mg/the chromate film of m2 was formed. The coating was applied to the plating steel plate by which chemical conversion was carried out, and the one quart paint film and the clear paint film were formed. When the polyester system plastic paint which added the strontium chromate of 5 mass % to the coating nonvolatile matter was used for one quart paint films, and desiccation thickness applied by the coverage used as 10 micrometers and was able to be burned at 230 degrees C, the enamel paint film and the clear paint film were formed. When the plastic paint of acrylic and an urethane system was used for one quart paint films, desiccation thickness applied by the coverage used as 1 micrometer, and was able to be burned at 150 degrees C. Moreover, titanium oxide was suitably added as a color pigment in the coatings for one quart paint films. For the comparison, the melting zinc (0.2%aluminum) plating steel plate, -5% aluminum plating steel plate of melting zinc, and -55% aluminum plating steel plate of melting zinc were used as a paint negative, and the one quart paint film was formed under the same conditions.

[0024] Each obtained paint steel plate blank test piece was started, and the accelerated corrosion test and the coin scratch trial were presented. In the accelerated corrosion test, after spraying 35-degree C 5% salt water on a test piece for 240 hours, the paint film blistering width of face of a bottom weld flash cutting plane and the cross-cut section was measured. Corrosion resistance was evaluated having used as x that to which the maximum of paint film blistering width of face exceeds O and 2-3mm for 2mm or less, and exceeds ** and 5mm for O and 3-5mm along a cutting plane. The cross-cut section estimated corrosion resistance, having used as x that to which the maximum of paint film blistering width of face exceeds O and 1mm or less for 0mm, and exceeds ** and 3mm for O and 2-3mm.

[0025] In the coin scratch trial, it let coin slide along the test piece front face, and the paint film got damaged, and the desquamative state was observed. Although the crack went even into the middle lamella of O and a paint film - the depths that to which a crack stops at the surface of a paint film, that in which ** and a paint film exfoliated that by which O and a substrate were slightly damaged with [which does not reach a substrate] the crack was scratched as x, and resistance was evaluated. In the test numbers 1-9 which used the Zn-aluminum-Mg system plating steel plate for the paint negative, paint film blistering was controlled also in any of a bottom weld flash cutting plane and the cross-cut section so that the results of an investigation of a table 2 might see. Moreover, since it scratches and resistance is excellent, it also turns out that the adhesion of the paint film to a substrate is excellent. The appearance of a paint steel plate was also equal as compared with the conventional two quart paint steel plate. on the other hand -- the test numbers 10-15 which used the hot-dip zinc-coated carbon steel sheet and the melting zinc-aluminum plating steel plate for the paint negative -- corrosion resistance -- and it scratched and all of resistance were inferior.

[0026]

表 2 : 各塗装鋼板の耐食性及び塗膜の引掻き抵抗性

試験 No.	塗 料			耐食性		引掻き 抵抗性	区 分
	樹脂系	着色顔料 含有量 (質量%)	防錆顔料 含有量 (質量%)	切断 端面	クロス カット部		
1	ポリエステル	50	5	◎	◎	○	本 発 明 例
2	ポリエステル	50	5	◎	◎	○	
3	ポリエステル	50	5	◎	◎	○	
4	ポリエステル	50	5	◎	◎	○	
5	ポリエステル	50	5	◎	◎	○	
6	ポリエステル	50	0	○	○	○	
7	ポリエステル	0	0	○	○	○	
8	アクリル	0	0	○	○	○	
9	ウレタン	0	0	○	○	○	
10	ポリエステル	50	5	△	×	×	比 較 例
11	ポリエステル	50	5	△	×	×	
12	ポリエステル	50	5	×	△	×	
13	ポリエステル	0	0	×	×	×	
14	アクリル	0	0	×	×	×	
15	ウレタン	0	0	×	×	×	

防錆顔料：ストロンチウムクロメート

着色顔料：酸化チタン（添加量は不揮発成分に対する比率）

引掻き抵抗性：コインスクラッチ試験での評価

[0027]

[Example 2] The cooling approach, cooling conditions, and board thickness were changed, and the effect the cooling rate of a plating layer affects the irregularity of a plating layer front face was investigated. As seen in the table 3 showing the result of having observed the front face of the obtained hot-dipping steel plate, in the test numbers 1-9 from which crystal grain with it was obtained, it is in the range whose surface roughness is 0.7-2.3 micrometers of Ra, and the plating layer by which detailed irregularity was attached to the front face was formed. [a quick cooling rate and] [detailed] On the other hand, detailed irregularity was obtained neither in the test numbers 12-16 from which a plating presentation differs, nor the test numbers 10-12 with a slow cooling rate, but it had stopped at 0.3-0.4 micrometers of surface roughness Ra.

[0028] Each hot-dipping steel plate was painted and burned like the example 1, and physical properties were evaluated. the test numbers 1-9 which were in the range whose irregularity of a plating layer front face is 0.7-2.3 micrometers of Ra so that the assessment result of a table 4 might see -- an example 1 -- the same -- corrosion resistance -- it scratched and the product with good resistance was obtained. on the other hand -- the test numbers 10-16 whose surface roughness was 0.3-0.4 micrometers of Ra -- corrosion resistance -- scratching -- any of resistance -- or both sides were inferior.

[0029]

表 3 : めっき組成及び冷却速度がめっき層表面の凹凸に及ぼす影響

試験 番号	めっき層の組成(質量%, 残部: Zn)				めっき層の 冷却速度 (℃/秒)	めっき層表面の 凹凸 Ra(μ m)	区 分
	Al	Mg	Ti	B			
1	6	3	0.02	0.08	2	0.7	本 発 明 例
2	6	3	0.02	0.08	10	1.1	
3	6	3	0.02	0.08	20	1.2	
4	6	3	0.02	0.08	50	1.7	
5	6	3	0.02	0.08	100	2.1	
6	6	3	0.02	0.08	500	2.3	
7	6	3	0.02	0.08	10	1.2	
8	6	3	0.02	0.08	10	1.2	
9	6	3	0.02	0.08	10	1.2	
10	6	3	0.02	0.08	0.5	0.4	比 較 例
11	6	3	0.02	0.08	0.1	0.3	
12	0.2	—	—	—	10	0.3	
13	5	0.3	—	—	10	0.3	
14	0.2	—	—	—	10	0.3	
15	0.2	—	—	—	10	0.3	
16	0.2	—	—	—	10	0.3	

[0030]

表 4 : 各種塗装鋼板の耐食性及び引掻き抵抗性

試験 番号	塗 料			耐食性		引掻き 抵抗性	区 分
	樹脂系	着色顔料 含有量 (質量%)	防錆顔料 含有量 (質量%)	切断 端面	クロス カット 部		
1	ポリエステル	50	5	◎	◎	○	本 発 明 例
2	ポリエステル	50	5	◎	◎	○	
3	ポリエステル	50	5	◎	◎	○	
4	ポリエステル	50	5	◎	◎	○	
5	ポリエステル	50	5	◎	◎	○	
6	ポリエステル	50	5	○	○	○	
7	ポリエステル	0	0	○	○	○	
8	アクリル	0	0	○	○	○	
9	ウレタン	0	0	○	○	○	
10	ポリエステル	50	5	◎	◎	△	比 較 例
11	ポリエステル	50	5	◎	◎	△	
12	ポリエステル	50	5	△	×	×	
13	ポリエステル	50	5	△	×	×	
14	ポリエステル	0	0	×	×	×	
15	アクリル	0	0	×	×	×	
16	ウレタン	0	0	×	×	×	

[0031]

[Example 3] Acid washing of the steel plate by which hot dipping was carried out was carried out under various conditions, and the effect acid-washing conditions affect the irregularity of a plating layer front face was investigated. In the test numbers 1-7 with which the remains of etching of a Zn2Mg phase were detected, the detailed irregularity of 1.8-3.3 micrometers of Ra was attached to the plating layer front face so that the results of an investigation of a table 5 might see. On the other hand, with the test numbers 8-12 from which a plating presentation differs, detailed irregularity was not obtained but surface roughness had stopped at Ra0.4micrometer.

[0032] Each hot-dipping steel plate was painted and burned like the example 1, and physical properties were evaluated. the test numbers 1-7 which were in the range whose irregularity of a plating layer front face is 1.8-3.3 micrometers of Ra so that the assessment result of a table 6 might see -- an example 1 -- the same -- corrosion resistance -- it scratched and the product with good resistance was obtained. on the other hand -- the test numbers 8-12 whose surface roughness was Ra0.4micrometer -- corrosion resistance -- it scratched and inferior to the both sides of resistance.

[0033]

表 5 : めっき組成及び酸洗条件がめっき層表面の凹凸に及ぼす影響

試験 番号	めっき層の組成(質量%, 残部: Zn)				酸洗液	めっき層表面の 凹凸 Ra(μ m)	区 分
	Al	Mg	Ti	B			
1	6	3	0.02	0.08	3% HCl	1.8	本 発 明 例
2	6	3	0.02	0.08	3% HNO ₃	2.4	
3	6	3	0.02	0.08	1% HF	2.9	
4	6	3	0.02	0.08	1% HF + 1% HNO ₃	3.3	
5	6	3	0.02	0.08	3% HCl	1.8	
6	6	3	0.02	0.08	3% HCl	1.8	
7	6	3	0.02	0.08	3% HCl	1.8	
8	0.2	—	—	—	3% HCl	0.4	比 較 例
9	5	0.3	—	—	3% HCl	0.4	
10	0.2	—	—	—	3% HCl	0.4	
11	0.2	—	—	—	3% HCl	0.4	
12	0.2	—	—	—	3% HCl	0.4	

[0034]

表 6 : 各種塗装鋼板の耐食性及び引掻き抵抗性

試験 番号	塗 料			耐食性		引掻き 抵抗性	区 分
	樹脂系	着色顔料 含有量 (質量%)	防錆顔料 含有量 (質量%)	切断 端面	クロス カット 部		
1	ポリエステル	50	5	◎	◎	○	本 発 明 例
2	ポリエステル	50	5	◎	◎	○	
3	ポリエステル	50	5	◎	◎	○	
4	ポリエステル	50	5	◎	◎	○	
5	ポリエステル	0	0	○	○	○	
6	アクリル	0	0	○	○	○	
7	ウレタン	0	0	○	○	○	
8	ポリエステル	50	5	△	×	×	比 較 例
9	ポリエステル	50	5	△	×	×	
10	ポリエステル	0	0	×	×	×	
11	アクリル	0	0	×	×	×	
12	ウレタン	0	0	×	×	×	

[0035]

[Example 4] Surface roughening of the plating layer was carried out by rolling and blasting with brushing and the dull roll using a grinding belt, and the hot-dip zinc-coated carbon steel sheet which attached irregularity to the plating layer front face was manufactured. When the front face of the obtained hot-dip zinc-coated carbon steel sheet was observed, as shown in a table 7, in the test numbers 1-7 with which the marks removed mechanically [aluminum phase or Zn phase] at a grinding belt or a

steel shot or the remains of pressing down with a dull roll was detected, the detailed irregularity whose surface roughness is 1.9-4.4 micrometers of Ra is attached to the plating layer front face, and the hard sludge of a Ti-B system, a Ti-aluminum system, and an aluminum-B system was also detected. On the other hand, with the test numbers 8-11 from which a plating presentation differs, although the detailed irregularity of surface roughness Ra1.1micrometer was detected, the hard sludge of a Ti-B system, a Ti-aluminum system, and an aluminum-B system was not detected only with soft Zn phase.

[0036] Each hot-dipping steel plate was painted and burned like the example 1, and physical properties were evaluated. the test numbers 1-7 with which it is in the range whose irregularity of a plating layer front face is 1.9-4.4 micrometers of Ra, and the hard sludge of a Ti-B system, a Ti-aluminum system, and an aluminum-B system was detected so that the assessment result of a table 6 might see -- an example 1 -- the same -- corrosion resistance -- it scratched and the product with good resistance was obtained. on the other hand -- the test numbers 8-11 without the hard sludge of a Ti-B system, a Ti-aluminum system, and an aluminum-B system -- corrosion resistance -- it scratched and inferior to the both sides of resistance.

[0037]

表 7 : 機械的な粗面化処理がめっき層表面の凹凸に及ぼす影響

試験 番号	めっき層の組成(質量%, 残部: Zn)				粗面化処理	めっき層表面の 凹凸 Ra(μ m)	区 分
	Al	Mg	Ti	B			
1	6	3	0.02	0.08	ダル圧延	1.9	本 発 明 例
2	6	3	0.02	0.08	ショットブラスト	2.5	
3	6	3	0.02	0.08	グリットブラスト	3.7	
4	6	3	0.02	0.08	ブラッシング	4.4	
5	6	3	0.02	0.08	ダル圧延	1.9	
6	6	3	0.02	0.08	ダル圧延	1.9	
7	6	3	0.02	0.08	ダル圧延	1.9	
8	0.2	—	—	—	ダル圧延	1.1	比 較 例
9	0.2	—	—	—	ダル圧延	1.1	
10	0.2	—	—	—	ダル圧延	1.1	
11	0.2	—	—	—	ダル圧延	1.1	

[0038]

表 8 : 各種塗装鋼板の耐食性及び引掻き抵抗性

試験 番号	塗 料			耐食性		引掻き 抵抗性	区 分
	樹脂系	着色顔料 含有量 (質量%)	防錆顔料 含有量 (質量%)	切断 端面	クロス カット 部		
1	ポリエステル	50	5	◎	◎	○	本 発 明 例
2	ポリエステル	50	5	◎	◎	○	
3	ポリエステル	50	5	◎	◎	○	
4	ポリエステル	50	5	◎	◎	○	
5	ポリエステル	0	0	○	○	○	
6	アクリル	0	0	○	○	○	
7	ウレタン	0	0	○	○	○	
8	ポリエステル	50	5	△	×	×	比 較 例
9	ポリエステル	0	0	×	×	×	
10	アクリル	0	0	×	×	×	
11	ウレタン	0	0	×	×	×	

[0039]

[Effect of the Invention] As explained above, the one quart paint film, the two quart paint film, etc. are formed through the chemical conversion coat on the Zn-aluminum-Mg system plating layer in which the paint steel plate of this invention attached detailed irregularity to the plating layer front face with distribution of a Ti-aluminum system, a Ti-B system, an aluminum-B system sludge, etc., grain growth control, acid-washing surface roughening, mechanical surface roughening, etc. Therefore, while the high corrosion resistance of Zn-aluminum-Mg system plating original is maintained, the adhesion of a paint film is also improved, it excelled and scratches, and resistance is presented. And even when adding a rust preventive pigment in coatings, the addition of a rust preventive pigment can be lessened, there is no coloring in a paint film, and good glossiness, corrosion resistance, weatherability, and moisture resistance are maintained, the corrosion resistance excellent in this paint steel plate -- and it scratches, resistance is utilized and it is used for extensive applications, such as inner package material, a sheathing material, mounting material, a shell plate for household-electric-appliances devices, and a partition.

[Translation done.]